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# Transient Techniques for Battery Impedance Measurements

## Small-Amplitude Exponential Perturbation Technique

Prepared by

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1 July 1981

AUG 13 1981

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Prepared for  
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**AIR FORCE SYSTEMS COMMAND**  
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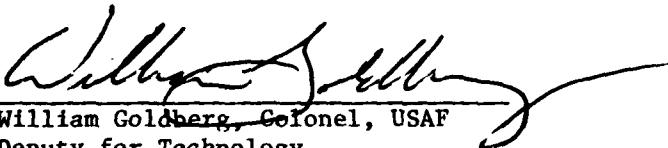
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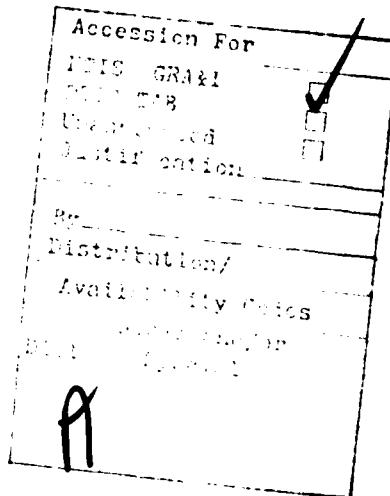
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20. ABSTRACT (Continue on reverse side if necessary and identify by block number) A perturbation technique is reported for measuring the impedance of battery cells under conditions of controlled potential. The small amplitude exponential perturbation (SAEP) technique is applicable over an extremely wide frequency range and appears to be the method of choice for measuring the impedance of battery cells that contain very little stored electrochemical energy.		

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## I. INTRODUCTION

The proper operation of battery cells invariably depends on a number of internal physical and chemical reactions occurring at rates that are sufficient to sustain cell performance. These reactions typically involve charge transfer processes at the electrodes, as well as diffusional transport of materials to the active electrode surfaces. Kinetic measurements permit determination of the relative importance of these processes in controlling cell performance. The most general method for making these kinetic measurements is to measure the electrical impedance of the battery cell as a function of frequency. The rates of the various processes that affect the cell voltage are inferred directly from the frequency dispersion of the cell impedance.

A number of techniques have been used to measure the impedance of battery cells. The most commonly used is that of applying a sinusoidally varying ac signal to the battery cell and monitoring the cell response in terms of amplitude and ac phase shift. This ac method is relatively easy to use, but if data are required over a wide frequency range or at very low frequencies, it becomes somewhat cumbersome. Other techniques for impedance measurements of battery cells incorporate perturbing functions other than sinusoidal ac. For example, in the galvanostatic transient technique<sup>1</sup> a step change in the current passing through the cell is applied, and the response of the cell to the current change is measured. The relationship between the change in cell current and the voltage response gives the cell impedance. This technique is particularly useful when the cell contains appreciable stored capacity, since in this case controlling cell current is much easier than controlling cell voltage. However, when the cell contains very little stored capacity, any measurement attempted under conditions of constant current may change the cell voltage by a large amount and thereby appreciably alter the chemical state of the cell. In this situation, it is desirable to employ a potentiostatic

<sup>1</sup>A. H. Zimmerman and M. R. Martinelli, Transient Techniques for Low Frequency Impedance Measurements, TR-0079(4970-10)-1, The Aerospace Corporation, El Segundo, Calif (6 October 1978).

technique that involves the application of a controlled perturbation to the cell potential.

We have developed and applied such a technique to battery cells. This technique is called small amplitude exponential perturbation (SAEP) and involves perturbing the cell voltage with a small amplitude (<5 mV) exponential signal while measuring the current response of the cell. Again, the cell impedance is obtained from the relationship between voltage and current. This technique can be used to measure the impedance of battery cells at any voltage or state of charge that is accessible to them, although very large currents (and power supplies) may be involved when the cell has appreciable active electrochemical capacity.

## II. THEORY OF SAEP

Any potentiostatic transient technique for measuring impedance employs a transient potential function  $V(t)$ . This potential function is applied as a perturbation to a battery cell that has the initial potential  $V_0$ . The cell current is initially  $I_0 + I_N(t)$ , where  $I_0$  is the steady-state current at  $V_0$ , and  $I_N(t)$  is any change in current resulting from depletion of the stored electrochemical capacity of the cell at the initial voltage. After the perturbation  $V(t)$  is applied, the current is  $I_0 + I_N(t) + I(t)$ . For this analysis to be correct, the amplitude of  $V(t)$  must be sufficiently small that  $I_N(t)$  does not change appreciably in response to  $V(t)$ . This means that typically  $V(t)$  should be less than 5 mV in amplitude. In addition, the time constant associated with  $I_N(t)$  must be much greater than that associated with  $I(t)$  so that they can be separated in time.

The impedance as a function of time is then directly given by Ohm's law

$$Z(t) = \frac{V(t)}{I(t)} \quad (1)$$

However, the cell impedance is more conveniently analyzed in the frequency domain. Laplace transformation of  $V(t)$  and  $I(t)$  permits us to obtain the impedance as a function of frequency.

$$Z(\omega) = \frac{V(\omega)}{I(\omega)} \quad (2)$$

where  $V(\omega)$  and  $I(\omega)$  are the Laplace transforms of voltage and current, respectively.

The digital Laplace transforms required are calculated from the voltage and current data,

$$F(\omega) = \int_0^\infty f(t) \exp(-j\omega t) dt = \sum_i \int_{t_i}^{t_{i+1}} f_i(t) \exp(-j\omega t) dt \quad (3)$$

which are digitized by computer into arrays having  $i$  data points, each corresponding to a given time. The function  $f_i(t)$  fits the data for  $f(t)$  in the interval  $t_i$  to  $t_{i+1}$  and may be any convenient function that fits the data. Functions used for  $f(t)$  include linear, quadratic, and exponential forms as follows.

1. Linear:  $f_i(t) = A_i t + B_i$

$$A_i = \frac{f(t_i) - B_i}{t_i}$$

$$B_i = \frac{[f(t_{i+1}) - t_{i+1}/t_i f(t_i)]}{1 - \frac{t_{i+1}}{t_i}} \quad (4)$$

2. Quadratic:  $f_i(t) = L_i t^2 + M_i t + N_i$

$$M_i = \left[ \frac{\Delta f_{12}}{\Delta t_{12}^2} \left( \frac{t_1^2}{t_{i+2}} - t_{i+2} \right) - \frac{\Delta f_{13}}{t_{i+2}} \right] \left[ 1 - \left( t_{i+2} \frac{\Delta t_{12}}{\Delta t_{12}^2} + \frac{t_1}{t_{i+2}} \left( \frac{t_1 \Delta t_{12}}{\Delta t_{12}^2} - 1 \right) \right)^{-1} \right]$$

$$L_i = \frac{\Delta f_{12}}{\Delta t_{12}^2} - M_i \left( \frac{\Delta t_{12}}{\Delta t_{12}^2} \right) \quad (5)$$

$$N_i = f(t_i) - L_i t_i^2 - M_i t_i$$

where

$$\Delta t_{12} = t_i - t_{i+1}$$

$$\Delta t_{12}^2 = t_i^2 - t_{i+1}^2$$

$$\Delta f_{12} = f(t_i) - f(t_{i+1})$$

$$\Delta f_{13} = f(t_i) - f(t_{i+2})$$

### 3. Exponential:

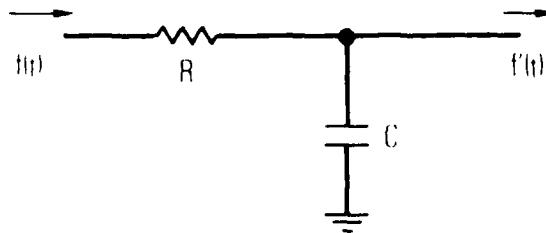
$$f_i(t) = C_i \exp(-a_i t) \quad (6)$$

$$a_i = \ln \left[ \frac{f(t_{i+1})/f(t_i)}{t_i - t_{i+1}} \right]$$

$$C_i = f(t_i) \exp(a_i t_i)$$

The exponential function of Eq. (6) gave the best results for all data that were not near a point where  $f(t)$  crossed zero. A listing of a Fortran program for doing the transformations that give the impedance is provided in the Appendix.

Actual experimental data contain noise; in particular, 60-Hz noise may pose a problem when small changes in voltage or current are being monitored. The simplest way to eliminate this kind of noise is with an RC filter.



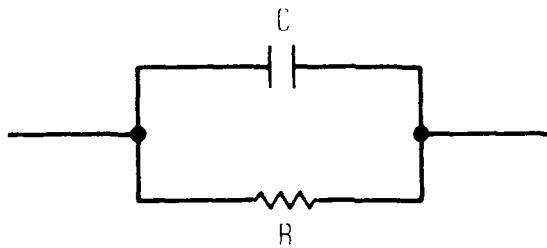
However, the transfer function of this filter must then be deconvoluted from the data. This is easily done in the frequency domain simply by multiplying the transformed function by the inverse filter function transform

$$f(\omega) = f'(\omega) (1 + j\omega\tau_F) \quad (7)$$

where  $\tau_F = RC$  is the filter time constant.

### III. RESULTS

The impedance of battery cells below 1 kHz is generally capacitive in nature, behaving as an equivalent parallel RC circuit where the values of R and C may have a complicated dependence on frequency. The results of an SAEP experiment on a simple dummy cell consisting of the RC circuit



where  $C = 1 \text{ F}$  and  $R = 10 \Omega$  are examined first. For simplicity, let us assume that  $V_0 + V_N(t)$ , the initial cell voltage, is zero. An increasing exponential perturbation having amplitude  $\alpha$  and time constant  $\tau$  is applied to the cell

$$V(t) = \alpha(1 - e^{-t/\tau}) \quad (8)$$

$V(t)$  and the current response of the dummy cell  $I(t)$  are indicated in Fig. 1 for  $\tau = 2\text{s}$ ,  $R = 10 \Omega$ , and  $C = 1 \text{ F}$ .  $I(t)$  is given by the relationship

$$I(t) = \frac{\alpha}{R} \left[ 1 - \left(1 - \frac{RC}{\tau}\right) e^{-t/\tau} \right] \quad (9)$$

Note that the values of R and C do not influence the time constant for current decay, but only control the amplitude of the current transient. From the time-dependent voltage and current functions, the impedance is calculated, with the results shown in Fig. 2 in the complex plane. The results in Fig. 2 agree with the theoretical result for the impedance

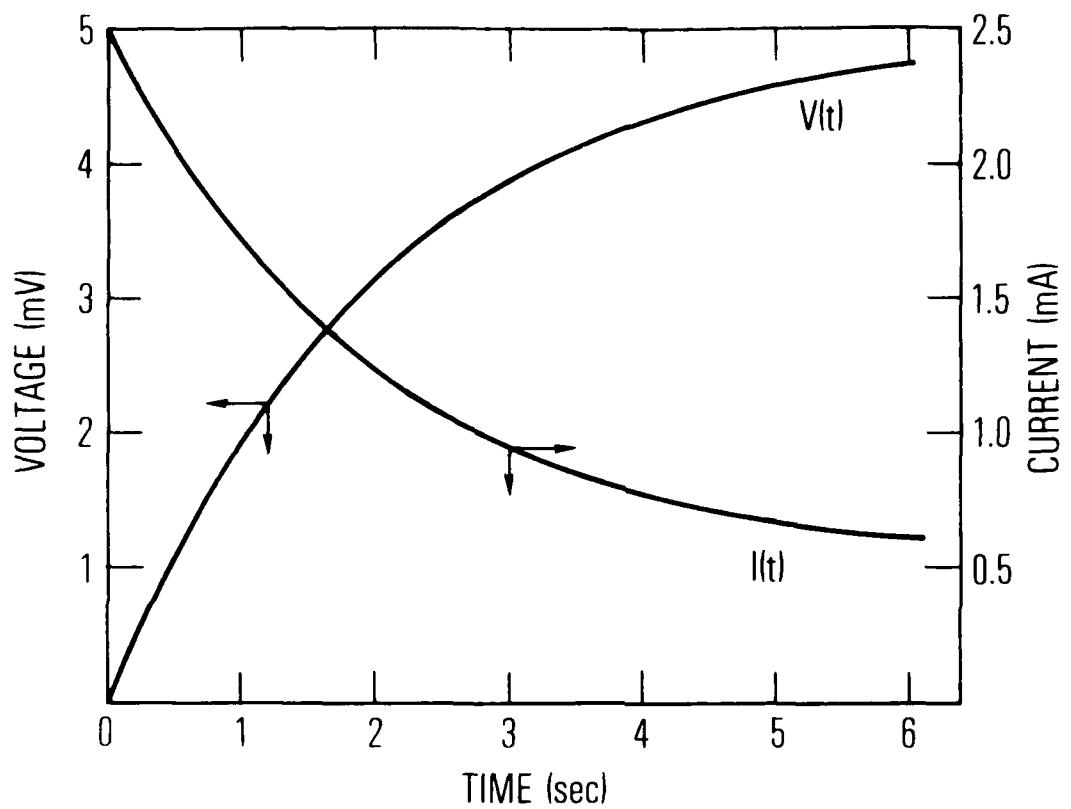


Fig. 1. Voltage Perturbation and Response Current for Dummy Cell

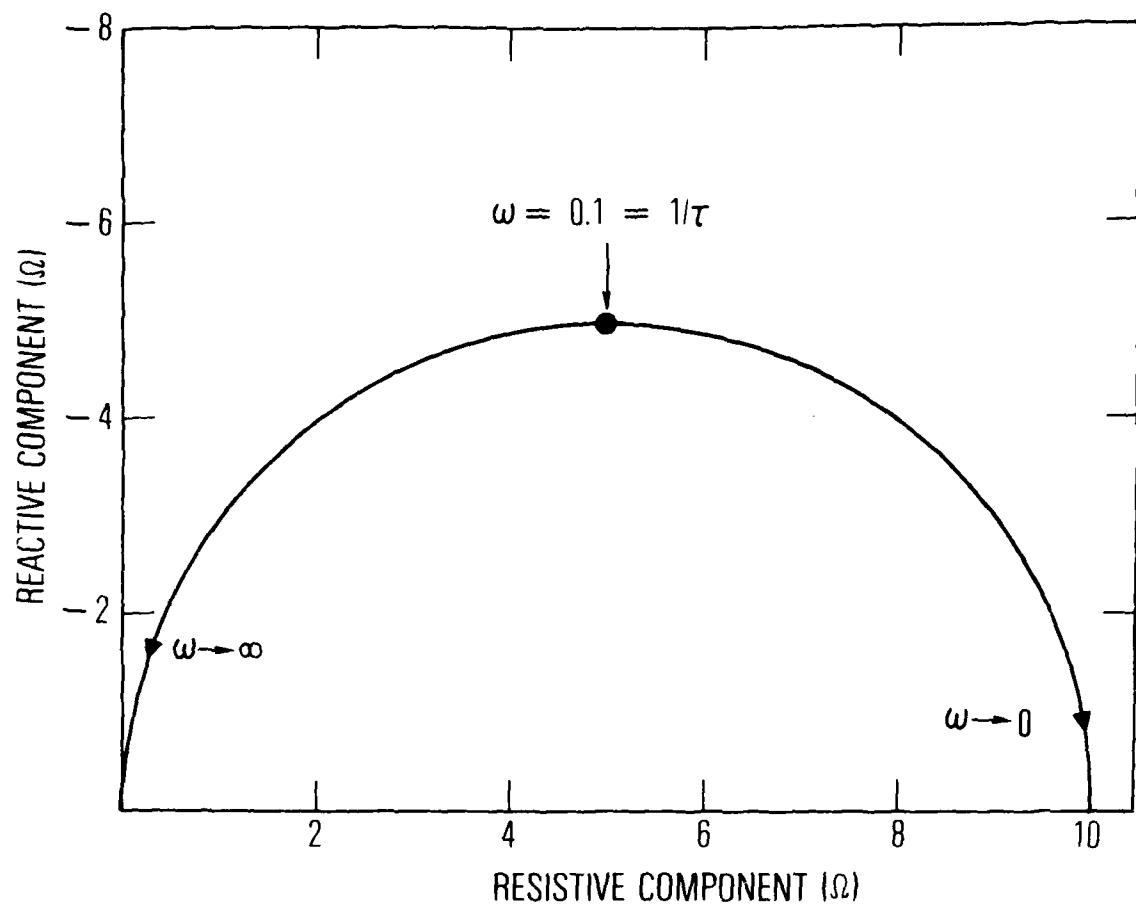


Fig. 2. Impedance of Dummy Cell from Data of Fig. 1

$$Z(\omega) = \frac{R}{1 + j\omega RC} \quad (10)$$

This simple example illustrates that the expected current response for a battery cell consists of a rapid rise to a maximum, followed by a decay to a steady-state current that is different from the initial current by the amount  $\alpha/R$ . The magnitude of the peak current is controlled by the relative time constants of the exponential perturbation and the cell, and is given by  $\alpha C/\tau$  in the preceding example. Thus, the experimental maximum transient current can be controlled simply by controlling the perturbation time constant.

The results obtained when an exponential perturbation is applied to a nickel cadmium cell are shown in Fig. 3. The nickel cadmium cell used was a 10-Ah prismatic cell, and the initial cell voltage was 0.5 V. The impedance is indicated in the complex plane in Fig. 4. In making these measurements, it was found that signal to noise became relatively poor unless the time constant of the applied perturbation was the same order of magnitude as the relaxation time for the battery cell. With this general requirement satisfied, the SAEP technique provides a convenient method for making impedance measurements on battery cells over an extremely wide range of frequencies, under conditions of battery operation for which potential control is acceptable.

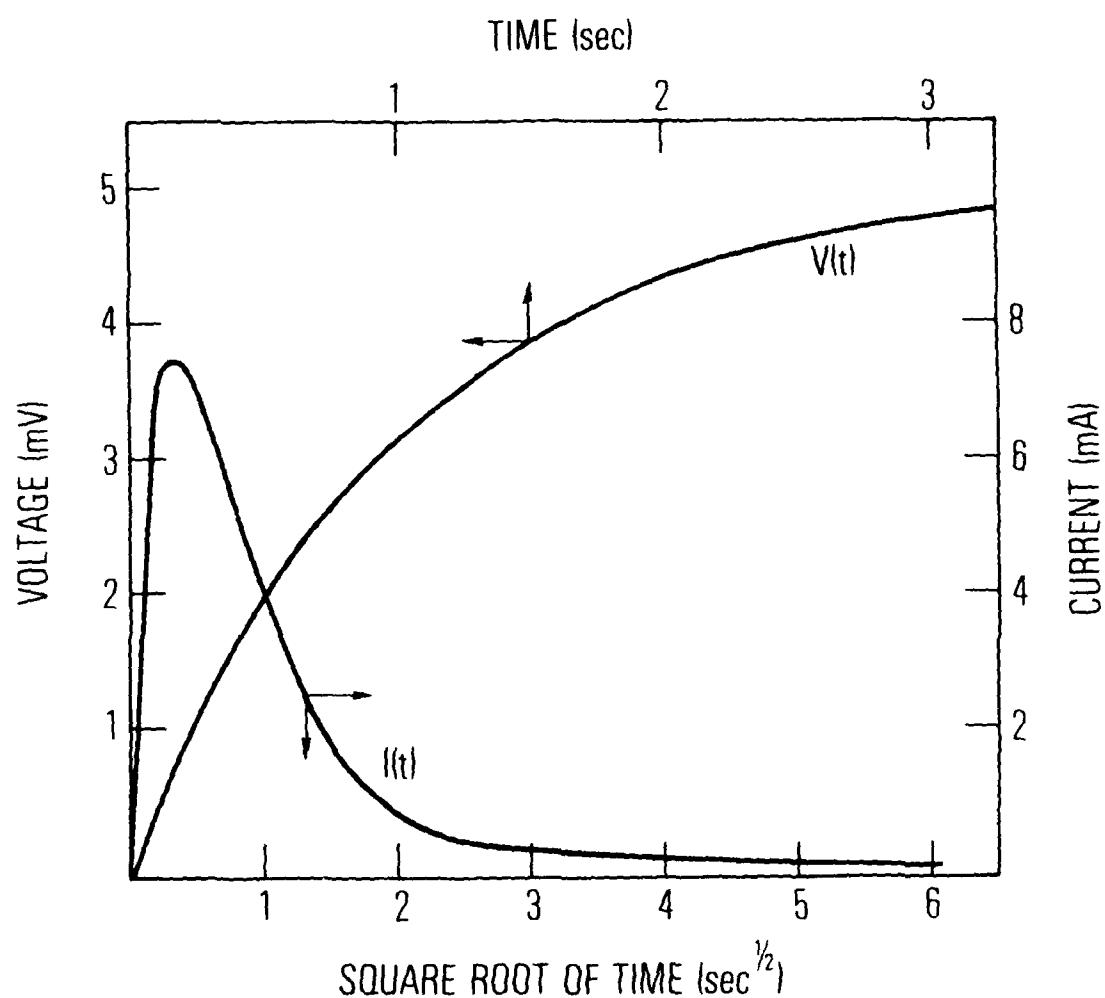


Fig. 3. Voltage Perturbation and Current Response for Nickel Cadmium Cell at 0.5 V

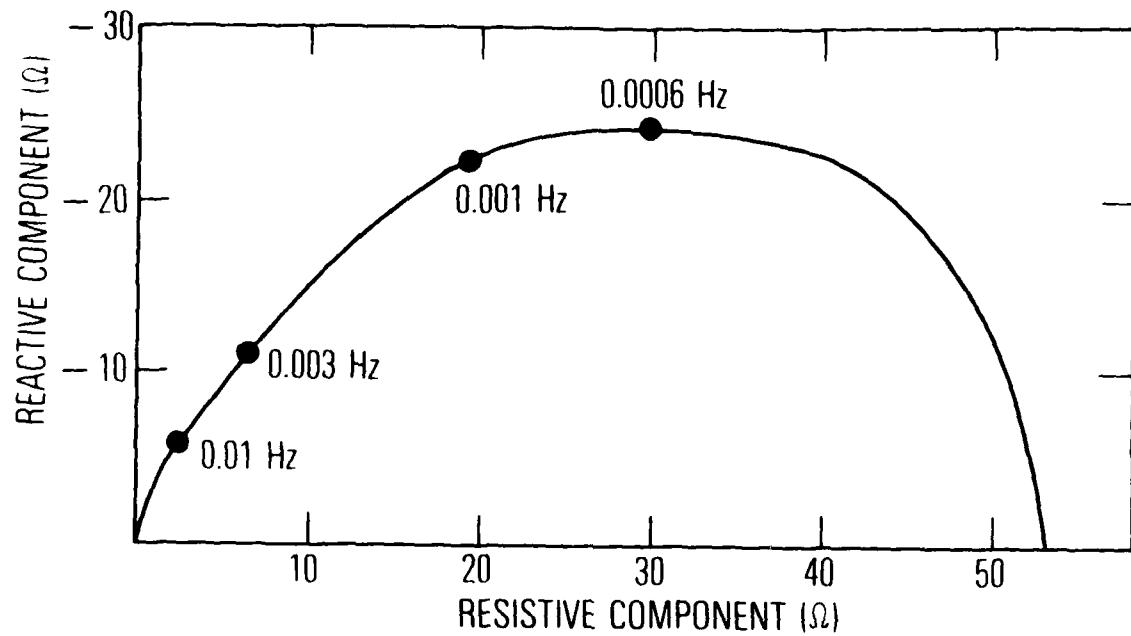


Fig. 4. Impedance of Nickel Cadmium Cell from Data of Fig. 3

#### IV. CONCLUSIONS

The SAEP technique has been developed and applied to measuring the impedance of battery cells under conditions of controlled potential. This appears to be the optimum method for measuring the impedance of battery cells that contain little stored electrochemical capacity.

APPENDIX

FORTRAN PROGRAM FOR SAEP IMPEDANCE CALCULATION

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PROGRAM SAFF (INPUT,OUT,UT,TAPES=INPUT,TAPES=OUTPUT) FREQUENCY FROM THIS PROGRAM CALCULATES IMPEDANCE AS A FUNCTION OF FREQUENCY FROM AN EXPONENTIAL VOLTAGE PERTURBATION AND ITS CURRENT RESPONSE USING THE LAPLACE TRANSFORMATION TECHNIQUE. A FILTER FUNCTION MAY BE INCLUDED IN THE CURRENT RESPONSE. AND IS DECONVOLVED FROM THE TRANSFORM.

DATA ARE INPUTS ARE EXPFITMENT IDENTIFICATION NUMBER  
 MPROB = NUMBER OF VOLTAGE DATA POINTS  
 NDATV = NUMBER OF CURRENT DATA POINTS  
 NDAEP = NUMBER OF PERTURBATION TIME CONSTANT IN SECONDS  
 TSAEP = NOMINAL PERIOD OF CURRENT PERTURBATION IN SECONDS  
 AMPV = AMPLITUDE OF EXPONENTIAL PERTURBATION IN V  
 FILTVC = TIME CONSTANT OF FILTER USED FOR VOLTAGE DATA (SEC)  
 FILTIC = TIME CONSTANT OF FILTER USED FOR CURRENT DATA (SEC)  
 VV(I), TSV(I) ARE ORDERED PAIRS CORRESPONDING TO TIME (SEC) AND  
 VV(I), TSV(I) ARE ORDERED PAIRS CONSISTING OF THE SQUARE ROOT OF  
 EXPONENTIAL VOLTAGE DATA (MV) AND SHOULD BE A NOMINALLY INFINITE ASTN.  
 EXPONENTIAL TSIC(I) IS ORDERED PAIRS CONSISTING OF THE SQUARE ROOT OF  
 XTIME AND CURRENT DATA (MA), AND SHOULD BE ZERO AT ZERO TIME  
 AND XTC(I) AT INFINITE TIME  
 COMMON/X(2,51),C(1,51),Y40(800),XS(4000),F(200),R2  
 COMMON/A(2,502),C(2,502),P(2,502),EPS(7),  
 COMPLEX ZH((2,03),VH,XIW,P,XFF,VFF  
 EQUIVALENCE (ORS, ZH)  
 DATA MUNIT, MTC, MNC, WBRK, MINC2, WFIN/V, 1.0, 4, 1.0, 1.0, 0.0 /  
 DATA SWITCH=9 GIVES IMPEDANCE CALCULATION ONLY  
 DATA SWITCH=1 GIVES IMPEDANCE CALCULATION AND FIT TO MODEL  
 SWITCH=0  
 CONTINUE  
 READ(5,201) MPROB, NDATV, NDATI, TSAEP, AMPV, FILTIC, FILTV  
 IF(EOF?) 1000, 301  
 WRITE(6,6000)  
 WRITE(6,6001) MPROB  
 WRITE(6,6002) TSAEP, FILTIC  
 WRITE(6,6003) AMPV, FILTIC  
 READ(5,200) (TSV(I), VV(I), I=1, NDATV)  
 READ(5,200) (TSI(I), XTI(I), I=1, NDATI)  
 WRITE(6,6004)  
 DO 302 J=1, NDATV  
 WRITE(6,6012) J, VV(J), TSV(J)  
 VV(J)=AMPV-VV(J)  
 TSV(J)=TSV(J)+\*\*2  
 WRITE(6,6013)  
 DO 303 J=1, NDATI  
 WRITE(6,6014) J, XTI(J), TSI(J)  
 WRITE(6,6015)



116  
117  
118  
119  
120  
121

60008 FORMAT(1X, [IMPEDANCE DATA])  
60009 FORMAT(8X,[DATA POINT],1X,[1/SQRT(OMEGA)],7X,[REAL 2],13X,[IMAGINA  
60010 \*RYZC8X,[FREQUENCY(HZ)],15,4(4X,F14.6),  
60010 FORMAT(1X),15,4(4X,F14.6),  
7000 FORMATT(1X),  
ENC

465

PROGRAM LENGTH INCLUDING I/O BUFFERS  
000745

FUNCTION ASSIGNMENTS

STATEMENT	ASSIGNMENTS	361	-	00033	320	-	000231	360	-	000267	
300	-	000354	430	-	000435	41000	-	000464	2004	-	000506
4001	-	000357	-	-	000513	60000	-	000515	-	-	000517
2002	-	000511	2003	-	000536	6004	-	000547	-	-	000557
6002	-	000524	6003	-	000567	6008	-	000573	6009	-	000577
6006	-	000561	6007	-	000615	-	-	-	-	-	-
6010	-	000561	7000	-	-	-	-	-	-	-	-
BLOCK NAMES AND LENGTHS	SAEP	-	000745	-	012742	A	-	001446	2	-	000010
VARIABLE	ASSIGNMENTS	AMPV	-	000667	A1	-	00000502	A2	-	00003502	
VAMP	-	0000670	AMPV	-	0000512	F	-	0012431501	FILTC	-	000071
C1	-	000002502	C2	-	0000673	I1	-	0000677501	INDATI	-	0000665
FILTV	-	00000672	MPROB	-	0000663	N	-	000000501	OBS	-	0000311501
J	-	00000674	NN	-	0000675	NPROB	-	000000503	SWITCH	-	0000062502
NDATV	-	00000664	P	-	0000676	R2	-	00012741501	TSI	-	0000113501
P	-	00000667	PEFS	-	00004503	RTSAEP	-	0000666	VH	-	0000643
S1	-	0001502	S2	-	00004502	VY	-	000066502	WHINC1	-	0000653
TSV	-	0001502	VFFF	-	0000653	WFIN	-	0000661	XFF	-	000051501
W	-	0001676	WBRK	-	0000657	XINIT	-	0000645	YHD	-	0000653
W1NC2	-	0001620	WINIT	-	0000655	XS	-	0000645	-	-	0000653
X1	-	0001620	XINIT	-	0000645	-	-	-	-	-	-
ZH	-	000131501	-	-	-	-	-	-	-	-	-
STAFF OF CONSTANTS	000470	-	-	-	-	-	-	-	-	-	-
START OF TEMPORARIES	000617	-	-	-	-	-	-	-	-	-	-
START OF INDIRECTS	000635	-	-	-	-	-	-	-	-	-	-
UNUSED COMPILER SPACE	007400	-	-	-	-	-	-	-	-	-	-

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SUBROUTINE MODEL(NPROB,0,6,NG,NQ),YMD(800),XSC(4000),F(200),RZ,
COMMON/A1/S1,C1/A2,S2,C2,VV(200),TSV(200),X1(200),TSI(200),
DCMPLX(X,ZW1,W2,ZC1,ZC2,Z1,Z2,G
COMPLEX X,CTANH
DATA UR,UI/1.,0.,0.,0./
A1=0.13
S1=0.43
C1=0.44
A2=0.45
S2=0.46
C2=0.47
RZ=0.48
NG2=NG/2
N62=12*NG/2
I=1,NG2
XX=X(I)
7C1=-UI*XX**2/C1
ZW1=S1*XX*(1-UI)*CTANH(A1*CSQRT(1UI)/XX)
Z1=ZC1*ZW1/(C1+ZW1)
Z2=ZC2*ZW1/(C2+ZW1)
72=9.2*EQ.0.) GO TO 110
7C2=-UI*XX**2/C2
ZW2=S2*XX*(1-UI)*CTANH(A2*CSQRT(1UI)/XX)
Z2=ZC2*ZW2/(C2+ZW2)
110 CONTINUE
111 GCONT=Z1+Z2+RZ
120 RETURN
END

```

112 113 114 115 116 117 118 119 120 121 122 123 124 125 126 127 128 129 130 131 132 133 134 135 136 137 138 139 140 141 142 143 144 145 146 147 148 149 150 151 152 153 154 155 156 157 158 159 160 161 162 163 164 165 166 167 168 169 170 171 172 173 174 175 176 177 178 179 180 181 182 183 184 185 186 187 188 189 190 191 192 193 194 195 196 197 198 199 200 201 202 203 204 205 206 207 208 209 210 211 212

#### SUBPROGRAM LENGTHS

000303

#### FUNCTION ASSIGNMENTS

110 - 000201

BLOCK NAMES AND LENGTHS  
MODEL - 000303 - 012742 A - 001446

VARIABLE ASSIGNMENTS	-	000003S12	CTANH	-	000276	C1	-	00002SC2
A1	-	000005S02	A2	-	000301	NG2	-	0001S12
C2	-	000055S02	FZ	-	000274	S02	-	000272
Q8S	-	000341S02	TSV	-	000629	S01	-	000271S01
TSI	-	000413S02	XX	-	000262	ZC2	-	0002673
VV	-	000065S02	Y10	-	000626	Z1	-	000000
XX	-	0003252	ZH2	-	0006266	Z2	-	000000
ZW1	-	0003256	-	-	-	-	-	-

START OF CONSTANTS  
000215

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SUBROUTINE PARTIAL(N,OGDN,NG,NQ)
COMMON/N, X(200), OBS(40), YMD(800), XS(4000), F(2000), R2
COMMON/2/NPROB, PEPSC(7)
COMMON/3/NDIM, N(1), OGDN(NG, NQ)
DO 120 I=1, NQ
PEPS12 = 5/ PEPSC(I)
NSAVE = 0(I)
NSAVE = NSAVE + PEPS12
CALL MODEL(NPRCB(I), OGDN(I, I), NG, NQ)
CALL MODEL(NPRCB(0), YMD(I), NG, NQ)
CALL MODEL(NPRCB(1), YMD(I), NG, NQ)
DO 120 J=1, NG
DO 120 J=1, NG
DO 120 J=1, NG
CONTINUE
120 RETURN
FNC

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SUBPROGRAM LENGTH	000105			
FUNCTION ASSIGNMENTS				
STATEMENT ASSIGNMENTS				
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START OF TEMPORARIES	000071			
START OF INDIRECTS	000075			
UNUSED COMPILER SPACE	011200			

SUBPROGRAM LENGTH	000143
FUNCTION ASSIGNMENTS	
STATEMENT ASSIGNMENT 1	- 000047
BLOCK NAMES AND LENGTH	- 000143
VARIABLE ASSIGNMENTS CTANH	- 000137
START OF CONSTANTS	000115
START OF TEMPORARIES	000123
START OF INDIRECTS	000137
UNUSED COMPILER SFA	011200

```

SUBROUTINE (FIXFRM (INDAT,I,VT,W,VH) PLACE TRANSFORM AT ANGULAR FREQUENC
Y THIS SUBROUTINE COMPUTES THE PLACE TRANSFORM AT ANGULAR FREQUENC
Y OF THE SET OF ORDERED PAIRS T AND VT CORRESPONDING TO TIME AND
Y FUNCTION VALUE AT THAT TIME. APPROACH ZERO AT INFINITE TIME AND CANNOT CROSS ZERO.
Y DIMENSION T(200),VT(200)
COMPLEX VH,CA,CI,C12,C11,CIP1
C14=INDAT-1
DO 100 I=1, IN
  IP=I*1.0
  IF(VT(IP).EQ.0.0) VT(I)=0.00001
  IF(VT(IP).LT.0.0) VT(I)=0.00001
  IF(VT(IP).LT.0.0) GO TO 150
  IF(VT(IP).LT.0.0) VT(I)=0.0
  IF(VT(IP).LT.0.0) VT(I)=0.0
  A=ALOG(VT(I))
  C1=CHPLX(A,W)
  CIP=C1*W-T(I)
  C1=CHPLX(C1,-W*T(I))
  VH=VH+(VT(I)*CEXP(C1)-VT(IP))*CEXP(CIP))/CA
  GO TO 100
  150 IF(T(I).EQ.0.0) T(I)=0.0001
  DT=(T(IP)-T(I))/(1-0T)
  B=(VT(IP)-DT*VT(I))/(1-0T)
  A=(VT(I)-B)/T(I)
  CA1=CHPLX(A,W)
  CI1=CEXP(-CA1+T(I))/CA1
  CIP1=CEXP(-CA1*T(IP))/CA1
  VH=VH+(CI1*(T(I)+1.0/CA1)-CIP1*(T(IP)+1.0/CA1))+B*(CI1-CIP1)
  100  VH=VH+VT(IP)*CEXP(CIP)/CA
  267  CONTINUE
  101  RETURN
  311  CONTINUE
  312  ENC

```

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113 114 115 116 117 118 119 120 121 122 123 124 125 126 127 128 129 130 131 132 133 134 135 136 137 138 139 140 141 142 143 144 145 146 147 148 149 150 151 152 153 154 155 156 157 158 159 160 161 162 163 164 165 166 167 168 169 170 171 172 173 174 175 176 177 178 179 180 181 182 183 184 185 186 187 188 189 190 191 192 193 194 195 196 197 198 199 200

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SUBPROGRAM LENGTH	000420
FUNCTION ASSIGNMENTS	
STATEMENT ASSIGNMENTS	
100 - 000255 101 - 000312 150 - 000122	
BLOCK NAMES AND LENGTHS	
LPXFRM - 000420	
VARIABLE ASSIGNMENTS	
A - E00415 R - 000417 CA1 - 000376	
CI - 000406 CIP - 000402 CI1 - 000410	
DT - 000416 T - 000413 IP - 000412	
START OF CONSTANTS	
000315	

